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The Structure and Transport of Water and Hydrated Ions Within Hydrophobic, Nanoscale Channels

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Abstract

The purpose of this project includes an experimental and modeling investigation into water and hydrated ion structure and transport at nanomaterials interfaces. This is a topic relevant to understanding the function of many biological systems such as aquaporins that efficiently shuttle water and ion channels that permit selective transport of specific ions across cell membranes. Carbon nanotubes (CNT) are model nanoscale, hydrophobic channels that can be functionalized, making them artificial analogs for these biological channels.

This project investigates the microscopic properties of water such as water density distributions and dynamics within CNTs using Nuclear Magnetic Resonance (NMR) and the structure of hydrated ions at CNT interfaces via X-ray Absorption Spectroscopy (XAS). Another component of this work is molecular simulation, which can predict experimental measurables such as the proton relaxation times, chemical shifts, and can compute the electronic structure of CNTs.

Some of the fundamental questions this work is addressing are: 1) what is the length scale below which nanoscale effects such as molecular ordering become important, 2) is there a relationship between molecular ordering and transport?, and 3) how do ions interact with CNT interfaces? These are questions of interest to the scientific community, but they also impact the future generation of sensors, filters, and other devices that operate on the nanometer length scale. To enable some of the proposed applications of CNTs as ion filtration media and electrolytic supercapacitors, a detailed knowledge of water and ion structure at CNT interfaces is critical.

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Introduction:

The properties of water and hydrated ions in confined systems have long been of interest to researchers. Biology operates on nanometer length scales, and the unique properties that water and ions exhibit on this scale often govern the functionality of biological systems. A prominent example of this is the aquaporin channel that regulates water transport in our cells (Fig. 1A). The combination of pore structure and residues in the pore interior causes water to adopt a configuration that facilitates rapid transport, but prevents proton transport. Carbon nanotubes (CNT) can be regarded as synthetic channels that share similarities with biological channels in terms of their size and hydrophobicity, and they can be selectively functionalized.(Chen *et al.* 1998; Dyke and Tour 2004) These properties motivated researchers to model water behavior in CNTs,(Hummer *et al.* 2001; Kalra *et al.* 2003) with the observation that water also adopts unique configurations in these channels (Fig. 1B), and transport rates are often enhanced relative to those in aquaporin channels. These enhanced transport characteristics were recently validated experimentally through the development of CNT membranes here at LLNL.(Holt *et al.* 2006)

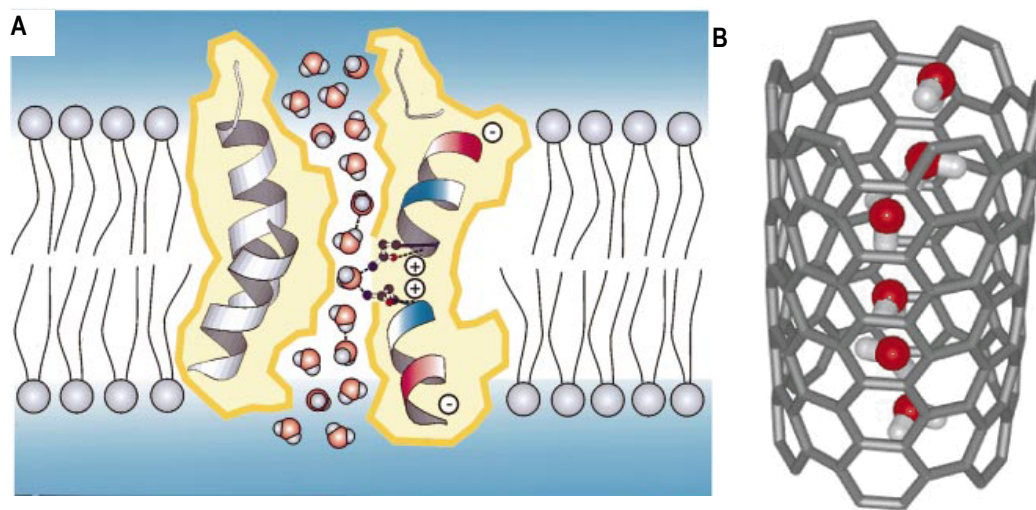


Figure 1. (A) Illustration of a natural aquaporin water channel, regarded as the “plumbing systems for cells”. Water is confined in the 2 nm restriction of this hourglass structure, adopting a single file structure. Water also experiences interactions with pore functionalities, preventing the formation of hydrogen bonds between water molecules, and thus blocking proton transport, which is the key to the biological function of this protein. Reprinted with permission from Ref. (Murata *et al.* 2000) (B) Illustration of water ordering phenomenon within a single wall CNT, attributed in part to confinement effects and the hydrophobicity of the surface. Reprinted with permission from Ref. (Hummer *et al.* 2001).

There are a number of open questions, however, that motivate the use of spectroscopic and modeling techniques to get a glimpse of how water and ions behave inside CNTs and at their interfaces. One fundamental question is: on what length scale do nanofluidic effects (e.g., one-dimensional molecular ordering) become important? Along related lines, is molecular ordering a pre-requisite for enhanced transport, or does water merely slip along the hydrophobic CNT surface, buffeted by a vapor barrier? The other fundamental question driving this project is: how do hydrated ions behave at CNT interfaces? This question is interesting not only because of the

biomimetic nature of CNTs, but because of its relevance to high-impact applications of CNTs as electrolytic supercapacitors and ion filtration media.

The techniques we propose to use are well suited to studying the details of water and ion structure on the nanometer length scale. Our previous results have demonstrated the power of NMR to provide unique structural and dynamical information about water in confined environments. Having pinpointed a proton NMR signature for confined water, (Chen *et al.* 2008) the pulsed field gradient technique can be used to determine the self-diffusivity of this confined water. (Stejskal and Tanner 1965) More recent work has shown the technique to be useful in studying freezing transitions of confined water (Matsuda *et al.* 2006) and how they differ from bulk water.

XAS is a technique that enables one to probe the local structure around almost any element in the periodic table, including the number and chemical identity of near neighbors and average interatomic distances of up to 5-6 Å. The position, shape and the near edge structure (pre and post edge) is a very sensitive probe of the valence of the absorbing ion, and chemical nature and arrangement of the closest coordinating ligands; this is commonly referred to as the X-ray Absorption Near-Edge Structure (XANES). The oscillation in the extended region of the edge can be used to obtain accurate local structural information (up to 2 or 3 shells) even for amorphous or liquid samples; this region is commonly referred to as the Extended X-ray Absorption Fine Structure (EXAFS). For example, XAS may be used in solution chemistry to study such problems as the hydration of calcium (II) and other large and highly charged metal ions. (Jalilehvand *et al.* 2001; Sandstrom *et al.* 2001)

Computational modeling has already proven an indispensable tool for studying confined water and ions, particularly before experimental nanofluidic platforms were available. Molecular dynamics (MD) studies have shown that the average number of hydrogen bonds decreases when compared with bulk water for CNTs ranging in size from 0.8-1.6 nm in diameter. (Gordillo and Marti 2000) Other studies have shown one-dimensional ordering of water molecules within 0.8 nm CNTs, leading to concerted, pulse-like movement of the molecules through the channel due to the tight hydrogen bonding network. (Hummer *et al.* 2001) Osmotically-driven transport of water through a model 0.8 nm SWCNT membrane has also been investigated, (Kalra *et al.* 2003) with predictions of semi-frictionless flow that is nearly independent of channel length, in stark contrast to macroscopic flow. Phase transitions of water within CNTs have been studied by MD, with the earliest of these studies revealing the formation of hexagonal and heptagonal ice nanotubes, albeit at relatively large applied axial pressures of 50-500 MPa. (Koga *et al.* 2001)

Results:

Our prior LDRD support has resulted in progress on both the experimental and modeling fronts. In collaboration with Julie Herberg and Prof. Yue Wu's group at UNC,CH, we succeeded in identifying a proton NMR signature associated with endohedral (interior) water in single wall CNT channels of 1 nm diameter. This has been a heretofore elusive goal in the NMR community, due to uncertainties and errors associated with probe tuning and background subtraction methods employed. The results of these studies were described in a manuscript submitted to *Nanoletters* that is currently under review. (Chen *et al.* 2008) Having identified this signature for endohedral water, experiments aimed at probing the dynamics of this confined water are now possible and are currently underway. In particular, we have determined that the water self-diffusivity in larger diameter CNTs (inner diameter > 5 nm) is similar to that of bulk water. Similar such measurements are planned on 1 nm diameter CNTs and smaller to determine the size scale below which deviations from bulk water properties occur.

Significant progress has also been made with XAS studies. In collaboration with SSRL, Extended X-ray Absorption Fine Structure (EXAFS) and X-ray Fluorescence (XRF) measurements have been carried out on bromide-treated CNTs. These studies have revealed the presence of a basic site on the CNTs (both single and multiwall) that selectively binds bromide (Br^-) over cations present in solution. EXAFS further reveals that this basic site is located at a concave, armchair site on the graphene edge and that it is general to a host of other graphitic materials, including activated carbon and graphite powder. A manuscript detailing this work has already been prepared and is planned for submission to *Nature Materials* this month. Despite decades worth of studies, fundamental questions about graphene chemistry remain, and these questions lie at the heart of the usage of activated carbons and potentially CNTs as ion filtration media. Utilizing unique, state-of-the-art facilities, we are now starting to answer some of these fundamental questions.

Computational modeling in collaboration with the Quantum Simulations Group (Schwegler and Huang) has revealed an upfield shift in the proton NMR spectrum for water confined within CNTs (relative to bulk water). These modeling results, employing nucleus-independent chemical shift methods, were qualitatively consistent with the experimental NMR results discussed above, and were significant as they provided additional validation for our assignment of a specific peak in the proton NMR spectrum to water confined within carbon nanotubes. Modeling of the distribution of hydrated ions within CNTs (Schwegler and Reed) has also revealed that halide species (Cl^- , Br^-) migrate to the CNT wall relative to cations (Na^+), due to their polarizability. This is a significant finding that potentially gives us insight into the observed affinity of Br^- for graphitic surfaces that we experimentally observed through the EXAFS studies described above.

It is also worth noting that this project has garnered the attention of researchers in the nanofluidics community and the principal investigator (Holt) was invited to write a review article surveying the various methods for probing nanoscale water. (Holt 2008)

Conclusions:

The additional year of partial funding requested should allow the team to continue experiments aimed at answering several fundamental scientific questions. Proposed NMR experiments should allow us to firmly establish the length scale at which nanoscale effects such as the formation of water chains (Hummer *et al.* 2001) or novel ice phases (Koga *et al.* 2001) occur, and the extent to which that impacts transport phenomena. XAS experiments, coupled with computational modeling, will help us better understand the nature of ion/CNT interactions and whether a basic site on the graphene edge binds all halide species (Cl^- , Br^- , and I^-) in the same fashion. These results will prove indispensable to enabling applications of CNTs in areas of energy storage and filtration.

References Cited

- Chen J, Hamon MA, Hu H, Chen YS, Rao AM, Eklund PC, Haddon RC (1998) Solution properties of single-walled carbon nanotubes. *Science* 282:95-98.
- Chen Q, Herberg J, Mogilevsky G, Wang HJ, Stadermann M, Holt J*, Wu Y* (2008) Identification of Endohedral Water in Single-Walled Carbon Nanotubes by ^1H NMR. *Nano Letters*, submitted February 24, 2008, under review, *corresponding authors
- Dyke CA, Tour JM (2004) Covalent functionalization of single-walled carbon nanotubes for materials applications. *Journal of Physical Chemistry A* 108:11151-11159.
- Gordillo MC, Marti J (2000) Hydrogen bond structure of liquid water confined in nanotubes. *Chemical Physics Letters* 329:341-345.
- Holt JK (2008) Methods for Probing Water at the Nanoscale. *Microfluidics and Nanofluidics*, accepted April 22, 2008.
- Holt JK, Park HG, Wang YM, Stadermann M, Artyukhin AB, Grigoropoulos CP, Noy A, Bakajin O (2006) Fast mass transport through sub-2-nanometer carbon nanotubes. *Science* 312:1034-1037.
- Hummer G, Rasaiah JC, Noworyta JP (2001) Water conduction through the hydrophobic channel of a carbon nanotube. *Nature* 414:188-190.
- Jalilehvand F, Spangberg D, Lindqvist-Reis P, Hermansson K, Persson I, Sandstrom M (2001) Hydration of the calcium ion. An EXAFS, large-angle X-ray scattering, and molecular dynamics simulation study. *Journal of the American Chemical Society* 123:431-441.
- Kalra A, Garde S, Hummer G (2003) Osmotic water transport through carbon nanotube membranes. *Proceedings of the National Academy of Sciences of the United States of America* 100:10175-10180.
- Koga K, Gao GT, Tanaka H, Zeng XC (2001) Formation of ordered ice nanotubes inside carbon nanotubes. *Nature* 412:802-805.
- Mao SH, Kleinhammes A, Wu Y (2006) NMR study of water adsorption in single-walled carbon nanotubes. *Chemical Physics Letters* 421:513-517.
- Matsuda K, Hibi T, Kadowaki H, Kataura H, Maniwa Y (2006) Water dynamics inside single-wall carbon nanotubes: NMR observations. *Physical Review B* 74:073415.
- Murata K, Mitsuoka K, Hirai T, Walz T, Agre P, Heymann JB, Engel A, Fujiyoshi Y (2000) Structural determinants of water permeation through aquaporin-1. *Nature* 407:599-605.
- Radovic LR, Bockrath B (2005) On the Chemical Nature of Graphene Edges: Origin of Stability and Potential for Magnetism in Carbon Materials. *J. Am. Chem. Soc.* 127:5917-5927.
- Sandstrom M, Persson I, Jalilehvand F, Lindqvist-Reis P, Spangberg D, Hermansson K (2001) Hydration of some large and highly charged metal ions. *Journal of Synchrotron Radiation* 8:657-659.
- Shirley EL (1996) Optimal basis sets for detailed Brillouin-zone integrations. *Physical Review B* 54:16464.
- Stejskal EO, Tanner JE (1965) Spin Diffusion Measurements - Spin Echoes in Presence of a Time-Dependent Field Gradient. *Journal of Chemical Physics* 42:288-&.